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A Practical Approach In Performing the Particle Size Analysis of a Camouflage Coating Utilizing Laser-Light Scattering Technology

by Philip Patterson and William Lum

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A Practical Approach In Performing the Particle Size Analysis of a Camouflage Coating Utilizing Laser-Light Scattering Technology

Philip Patterson and William Lum
Weapons and Materials Research Directorate, ARL

Abstract

This technical report presents the results of an analytical research study performed at the U.S. Army Research Laboratory (ARL), Aberdeen Proving Ground (APG), MD. The focus of the work centers on the instrument setup and operation for performing particle size determinations on a polydispersed, camouflage paint conforming to the U.S. Department of the Army Military Specification MIL-C-53039A, "Coating, Aliphatic Polyurethane, Single Component, Chemical Agent Resistant." The analyses are graphically displayed and are provided with a brief explanation summarizing the results. A short description of merited future work is also mentioned.

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1. Introduction

An important step in the processing of camouflage coatings is the dispersion of the pigment particles within the resinous component of the system. If the quality of the dispersion is poor, the appearance and protective properties of the coating can be adversely affected.

The size of the pigment particles within dispersion can be measured in a variety of ways [1–3]. In this study, a laser-light scattering particle size analyzer was selected to perform the particle size determinations. Previous work conducted by the authors presented a basic introduction to the analytical technique and summarized a few preliminary analyses of coating materials [4].

To improve upon this initial effort, additional analyses were performed in an attempt to resolve some of the variability discovered during the initial trial runs. This report reviews some of these findings with a focus on the importance of proper instrument setup and operation.

2. Approach

The particle size analyses were performed using a Horiba LA-900 (Horiba Instruments, Irvine, CA) equipped with a 632.8-nm helium-neon laser and a tungsten light source with a blue filter. A forward-positioned photodiode array detector combined with a series of smaller wide-angle detectors receives the scattered light signals. Once detected, the optical scattering data is converted to a particle size distribution using a proprietary deconvolution routine designed by the vendor. The software used to collect the data and perform the conversion is compatible with Windows applications and requires the use of a high-speed (486/33 mHz) desktop computer. Samples were analyzed in a quartz fraction cell accessory capable of holding 15 ml of liquid. The cell holder is equipped with a variable speed, magnetic stirrer for keeping the particles suspended.

3. Experimental

A camouflage (383 Green) topcoat conforming to the military coating specification MIL-C-53039A, “Coating, Aliphatic Polyurethane, Single Component, Chemical Agent Resistant,” [5] was selected for the analyses. The “wet” coating sample contained a total pigment content of 34% by weight. All of the pigment particles were composed of inorganic compounds and were well dispersed in the coating matrix. The coating was packaged in a 1-qt metal container. To ensure coating homogeneity, the quart can was shaken vigorously for a minimum of 5 min on a mechanical paint shaker before an aliquot was taken. Samples were prepared by pipetting approximately five drops of the coating from the original 1-qt can into a disposable microcentrifuge tube and diluting with methyl ethyl ketone (1:2). The tube was then capped and gently shaken. A few drops of the diluted solution were pipetted into the fraction cell filled with methyl ethyl ketone and stirred immediately to prevent settling.

4. Results and Discussion

4.1 Stirring Speed Selection. Figure 1 represents an initial analysis of the coating material with the stir speed control set at the halfway position. As shown, the sample displays the characteristics of a bimodal distribution with particle sizes ranging from approximately 0.4 μ to 85 μ.

However, when the stir speed is adjusted to the near maximum position, the particle size distribution changes, as seen in Figure 2.

The appearance of additional signals occurring above 100 μ is due to air bubbles generated within the fraction cell by stirring the sample too vigorously. This is easily confirmed by removing the cell from the instrument and visually examining the solution for the presence of small bubbles. The speed required to keep the sample particles suspended without introducing air bubbles depends largely on the properties (i.e., viscosity) of the dispersion itself. The proper

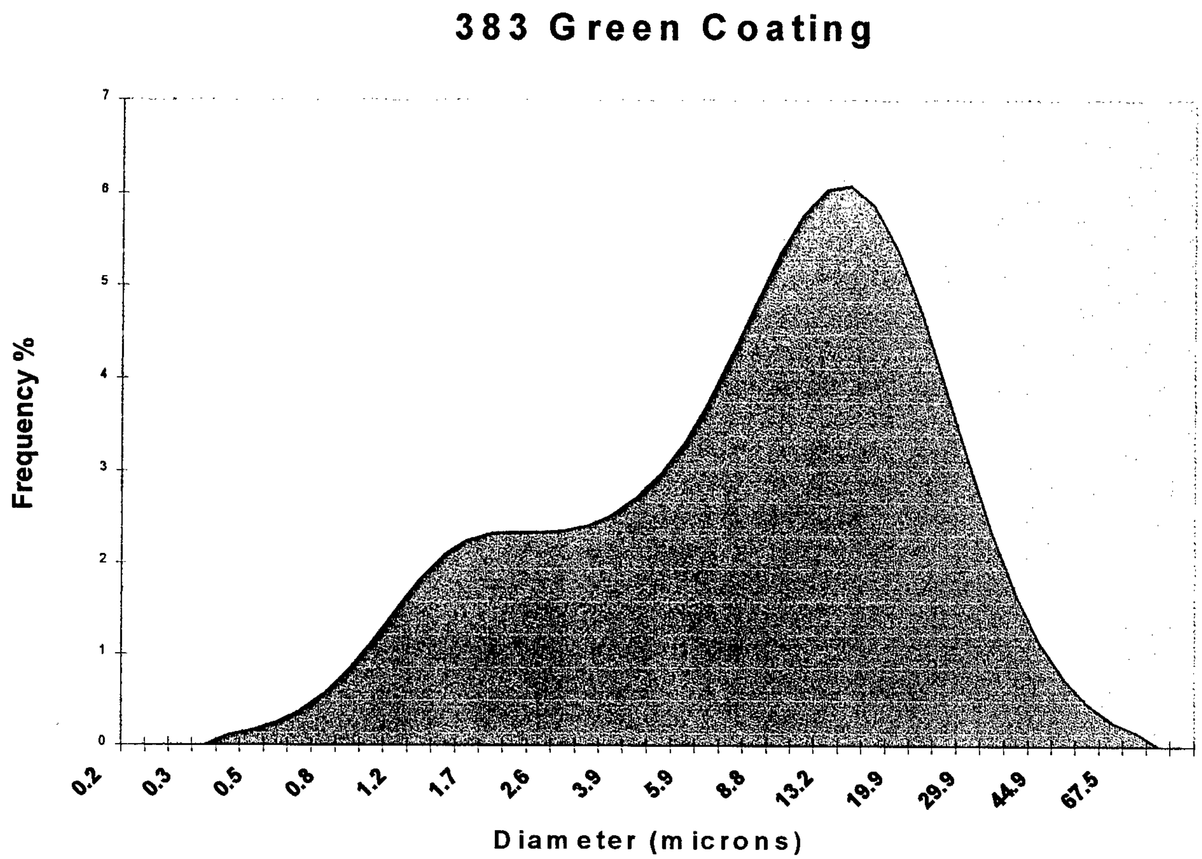

Figure 1. Particle Size Distribution of 383 Green Coating.

stir adjustment can be established by performing a few analyses at varying speeds. This can be done rather quickly, since the analysis time for each run is less than a minute.

4.2 Detector Alignment. Another example of extraneous data appearing in the particle size distribution is shown in Figure 3.

At first glance, this may appear to be caused by large air bubbles formed by fast stirring. However, it was found that the "false" signal was not dependent upon stir speed. It appeared and sometimes randomly disappeared, even when the sample was not being stirred. In this case, it was discovered that over time the array detector had drifted just slightly out of alignment, thereby changing the optical path. This became apparent by a flashing on and off of one of the light detector sensors during the analyses. Factors that can alter the path include

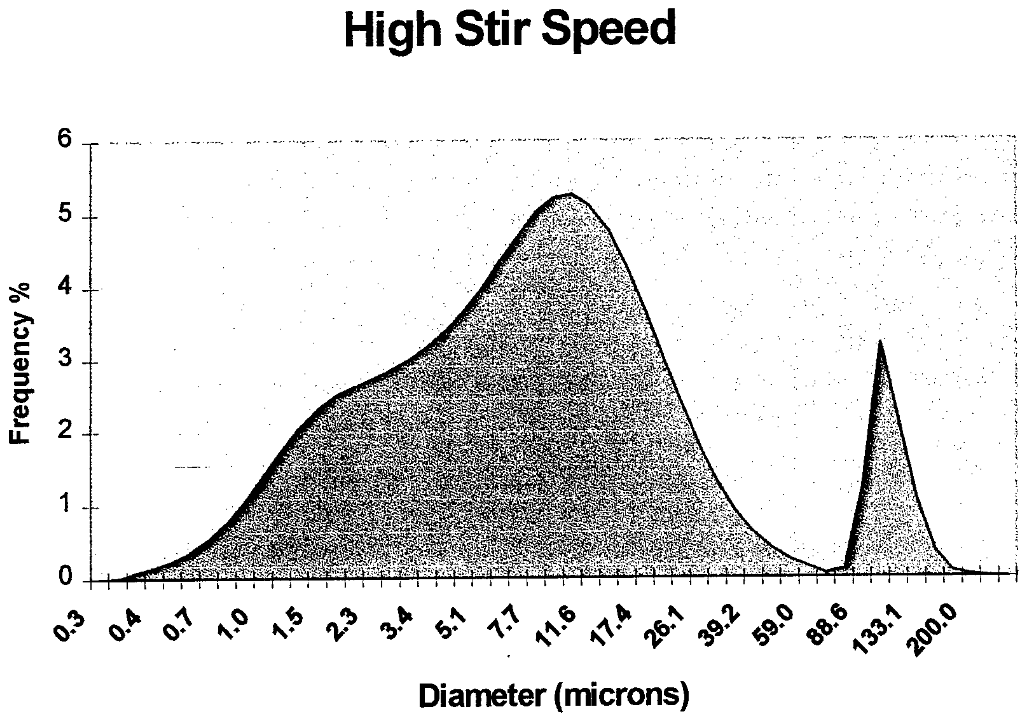

Figure 2. Particle Size Distribution of 383 Green Coating (Fast Stirring).

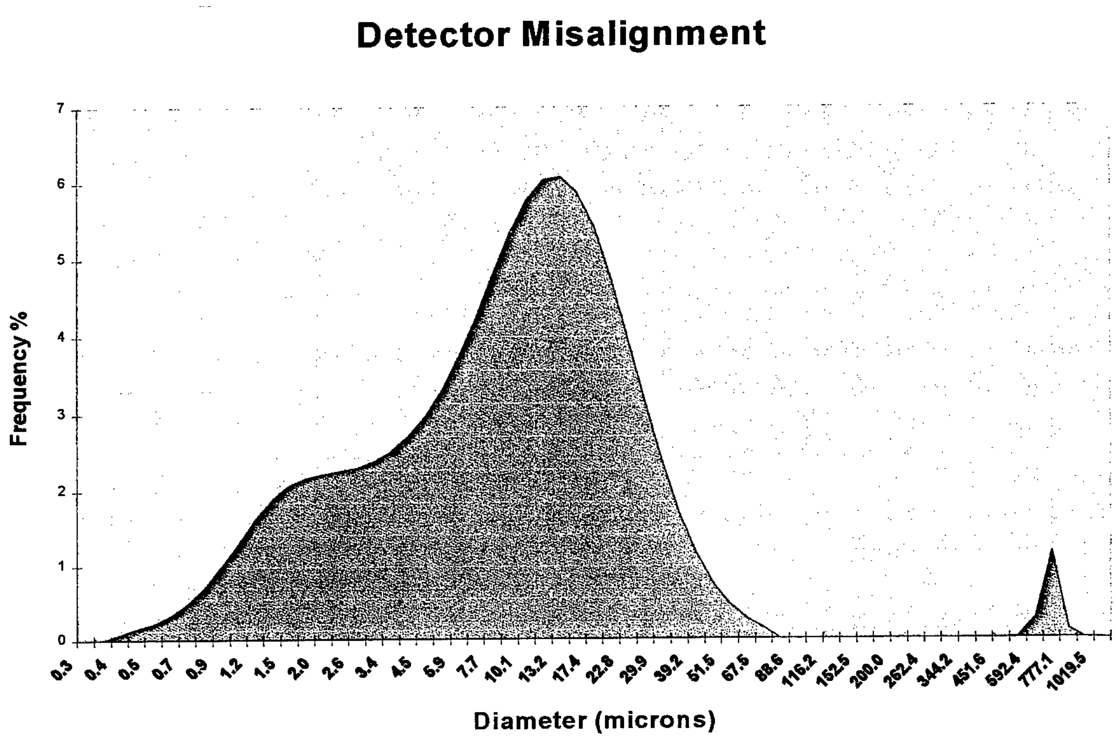

Figure 3. Effect of Misaligned Detector on Particle Size Distribution.

room-temperature variations, changes in the composition of the dispersing liquid, misplacement/replacement of the fraction cell, or movement of the optical bench. The problem was corrected by thoroughly cleaning the fraction cell and re-performing the detector alignment routine. The manufacturer recommends that the alignment be checked at regular time intervals and/or when a different series of analyses is to be performed.

4.3 Refractive Index Selection. Light scattering is an optical measurement, and therefore, the optical properties (i.e., Refractive Index [RI]) of the particles should be considered before analysis. The Horiba measurement software provides a fixed listing of index values from which the user can select. A value must be chosen in order for the software to perform the deconvolution of the detected light scattering data into a particle size distribution. For our coating sample, a wide range of RIs was selected to evaluate the effect on the resulting distribution. Table 1 summarizes the impact of a few of these index selections upon some of the commonly reported particle size characterization values.

Table 1. Refractive Index Changes

Index Setting	Median (μ)	Mean (μ)	% by Volume (>5 μ)	% by Volume (>10 μ)	% by Volume (>25 μ)
2.64–2.88i	8.10	10.43	65.2	41.4	7.6
1.90–2.98i	8.29	10.58	66.2	42.2	7.7
1.61–3.02i	8.35	10.65	66.5	42.5	7.8
1.39–2.75i	8.27	10.56	66.1	42.1	7.6
1.23–3.00i	8.15	10.51	65.4	41.7	7.7
0.26–2.46i	8.12	10.41	65.3	41.4	7.5

For this coating sample, it can be seen that the index setting has little effect upon the distribution results. This is best explained by examining the properties of the pigment particles themselves. The particles are:

(1) Very large with respect to the laser-light wavelength (0.632 μ).

(2) Opaque.

(3) Nonspherical.

In this instance, the majority of light scattering is due to particle edge effects, or Fraunhofer Diffraction. The importance of the particles' optical properties is minimized because there is little interaction between the light and the particles themselves. When Fraunhofer Diffraction dominates as the main light scattering phenomenon, a particle and a pinhole of the same size will produce the same diffraction pattern. As a matter of good practice, however, the refractive index selection should be chosen as close as possible to the actual RI of the particles. When there is a mixture of different particles, as in this sample, the RI of the predominant component is usually selected. Selection of RI values becomes more critical in performing the deconvolution computation when the particles are small (relative to the wavelength of the light source), spherical, and transparent. This is when there is a significant interaction between the light and the particles and the scattering effects become more complex.

4.4 Deconvolution Algorithms. The conversion of the scattered light patterns into an actual particle size distribution requires a deconvolution algorithm that in this case is written into the measurement software. The algorithmic routine is often vendor specific and is tailored around the optical configuration of the instrumentation. The Horiba LA-900 software uses an iterative, model-independent approach. The routine does not assume a "best fit" of the data to a predetermined distribution model. Instead, it performs a series of successive comparisons of the measured data to that of calculated distributions. The process eventually iterates the data toward the "real" particle size distribution curve of the material. The analyst chooses the number of times the algorithm performs these iterations. Figures 4–6 demonstrate how this parameter setting can affect the appearance of the particle size distributions.

This coating sample exhibits the characteristics of a very broad particle size distribution – greater than 1 decade. For this reason, a lower number of iterations, as shown in Figures 4 and 5, are recommended when performing the deconvolution computation. If a larger number are used,

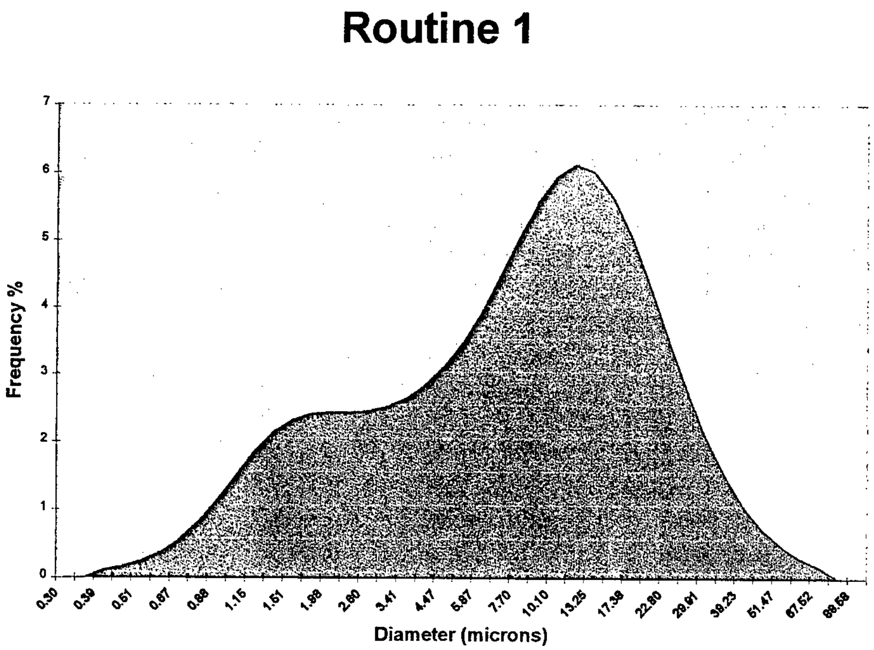

Figure 4. Deconvolution Algorithm Using ~ 10 Iterations.

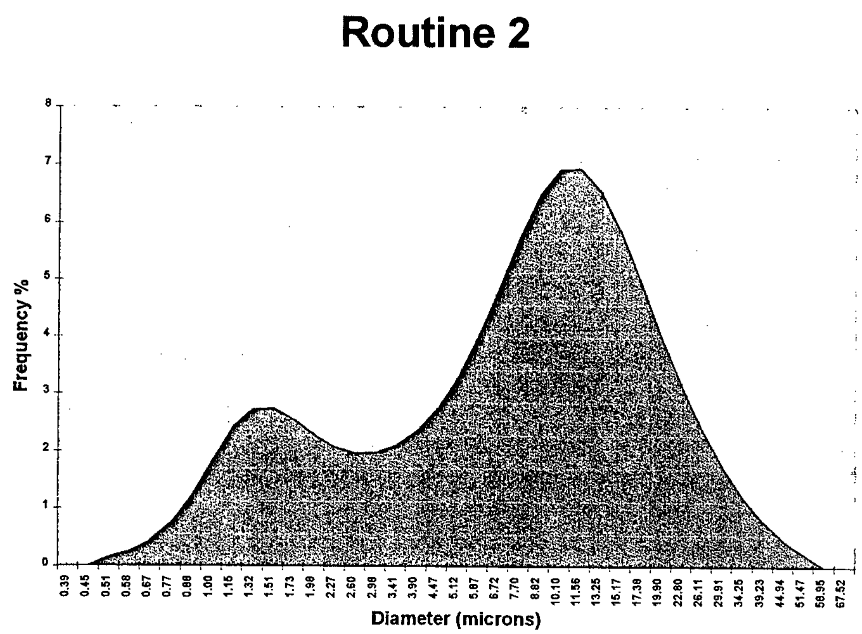

Figure 5. Deconvolution Algorithm Using ~ 40 Iterations.

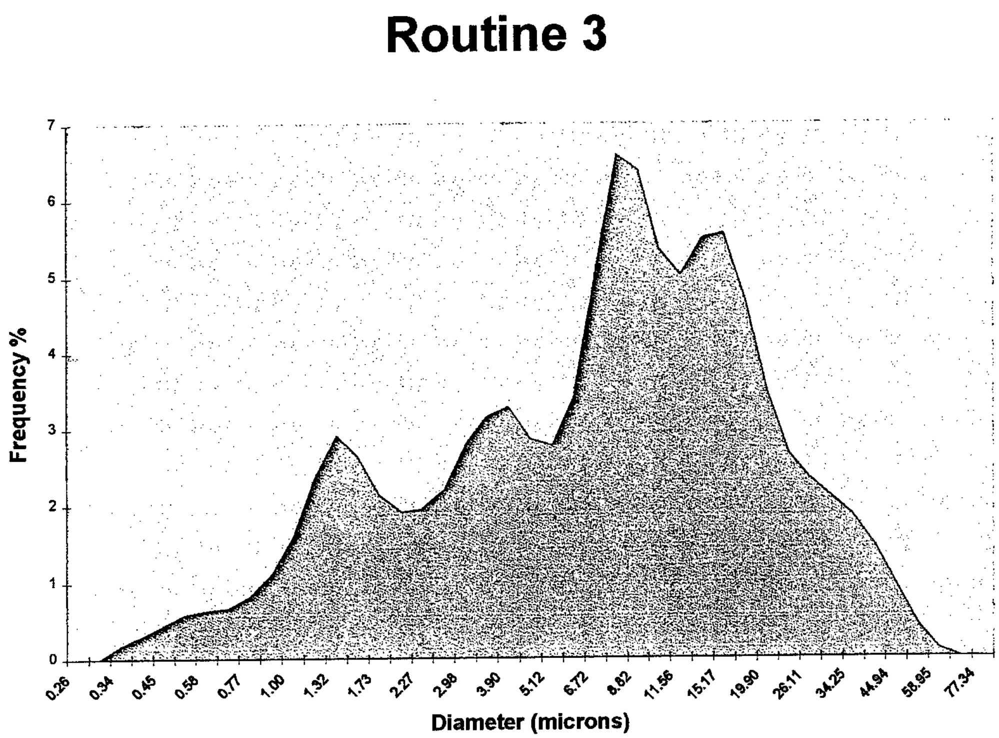

Figure 6. Deconvolution Algorithm Using ~ 150 Iterations.

as in Figure 6, the shape of the distribution becomes distorted due to an overamplification of detector noise and extraneous signals. The higher setting is recommended only under the following conditions:

(1) The sample exhibits a single mode with a very narrow distribution.

(2) The sample is truly multimodal, and the modes can be well resolved with the chosen deconvolution routine.

4.5 Averaging Multiple Distributions. Trial runs were made to ascertain how well a single operator could repeat an analysis. Table 2 presents the results of 10 separate determinations, all performed under the same experimental conditions.

Table 2. Repeatability of Particle Size Analysis

Trial No.	Median (μ)	Mean (μ)	% by Volume (>20 μ)	Trial No.	Median (μ)	Mean (μ)	% by Volume (>20 μ)
1	7.90	10.19	12.2	7	8.07	10.63	13.3
2	8.29	10.58	13.2	8	8.64	11.64	16.0
3	9.75	11.91	16.4	9	8.15	10.32	12.5
4	8.86	10.39	11.5	10	8.82	11.34	11.8
5	7.13	9.12	9.6	Average	8.36	10.74	13.4
6	8.02	11.24	14.1	Standard Deviation	0.703	0.818	2.09

Each of the previous analyses was stored as separate a data file. This is important when using another key feature of the instrument's software. After performing multiple particle size determinations, the operator can choose to average up to four individual data files.

An example of this "averaging" function is shown in Figure 7.

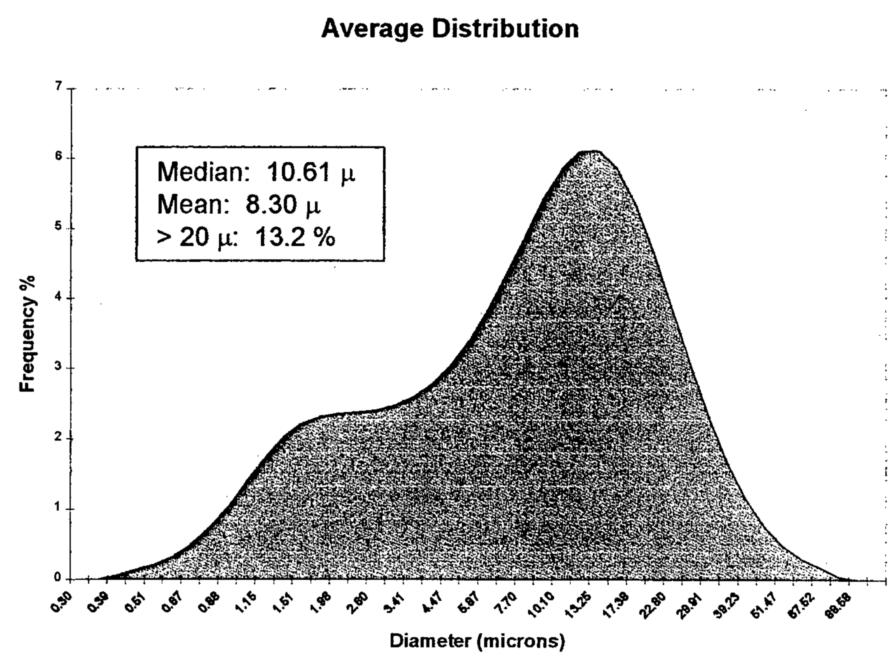

Figure 7. Average Distribution of Four Determinations.

In this example, Trial Nos. 1, 2, 9, and 10 were randomly selected. The newly derived particle size distribution curve is quite similar in appearance to the original distribution (Figure 1). Additionally, the statistical parameters (i.e., mean, median, etc.) agree well with those of the averaged data calculated for all 10 determinations (Table 2). This "averaged" file can now be saved as a control or reference distribution when future analyses are performed on revised formulations or on similar coatings products.

5. Conclusions

Laser-light scattering shows promise as a reliable method for determining the particle size distribution of camouflage coatings products. The analysis can be performed quickly without the generation of large quantities of hazardous waste. As with any new laboratory practice, the operator should be fully aware of the capabilities and potential problems associated with the technique. In this report, a number of practical examples have been presented to reinforce this concept. Note that the development of expertise in instrument operation is just one phase of a quality particle size analysis. Knowledge of the coating's background and preparation are also paramount in obtaining good characterization data. This could be the focus of future work. Also of interest would be the analysis of other camouflage coatings in other colors containing different pigment compositions.

6. References

1. Barth, H. G. *Modern Methods of Particle Size Analysis*. New York: John Wiley & Sons, 1988.

2. Allen, T. *Particle Size Measurement*. London: Chapman & Hall, 4th Edition, pp. 10–27, 1990.

3. McGarvey, M., D. McGregor, and R. B. McKay. "Particle Size Analysis by Laser Diffraction in Organic Pigment Technology." *Progress in Organic Coatings*, vol. 31, issue 3, pp. 223–228, July 1997.

4. Patterson, P., and W. Lum. "Laser Scattering Particle Size Distribution Analyses of Pigments." ARL-TR-1786, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, September 1998.

5. Department of the Army. *Coating, Aliphatic Polyurethane, Single Component, Chemical Agent Resistant.* MIL-C-53039A, Washington, DC, 1989.

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